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(54) Title: RECEIVER MEDIUM FOR INK JET PRINTING

(57) Abstract

A receiver medium for use with oil–based ink jet printing ink comprises a substrate having an ink receiving surface bearing a coating of crosslinked polymer comprising polyalkene, e.g. butadiene crosslinked with melamine–formaldehyde resin. The coating is capable of absorbing oil and use of such a coating can thus enable oil–based inks to be printed successfully onto non–absorbent substrates, including optically transparent media such as polyethylene terephthalate films, e.g. for the production of transparency sheets for use in OHPs, in a way that has not hitherto been possible. The substrate may alternatively be absorbent and may itself act to absorb some of the oil from applied ink. The invention also covers a method of making the medium and a method of printing using the medium.

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Title: Receiver medium for ink jet printing

## Field of Invention

This invention concerns a receiver medium for use in ink jet printing, particularly for use with oil-based ink jet printing inks, and also relates to a method of making such a medium and a method of printing using such a medium. The term "oil-based ink" is used to mean a substantially non-aqueous ink composition employing solvents or diluents other than water and containing one or more oils.

## Background to the Invention

Ink jet printing is a widely used printing technique. In general, ink jet printing inks are water-based compositions, and such inks are widely used in a range of different ink jet printers, for commercial, office and domestic use, including desk-top printers. Oil-based ink jet printing inks comprising a low viscosity dispersion of pigment in non-volatile non-aqueous diluent comprising a major amount of aliphatic hydrocarbon (oil) and a minor amount of oleyl alcohol are also known; see WO 96/24642. Such oil-based inks have the advantages of enabling printing to be performed very rapidly and also producing a water-resistant end product. Such inks are not, however, widely used commercially, and currently the only commercially available ink jet printers designed to use oil-based inks are wide-format printers designed to print on large rolls of paper, typically about 1 metre in width. Because oil-based inks are non-volatile, the diluent must be absorbed or otherwise permanently accommodated by the receiver medium to produce an acceptable print. Such oil-based inks produce good results when printing on paper and similar absorbent materials, with the oil being rapidly absorbed by the porosity of the paper or other material while leaving the pigment near the surface. However, such oil-based inks are not capable of providing adequate prints on non-absorbent media eg transparent media (which cannot have macroscopic pores as these scatter light and render the material opaque), and so cannot be used, for example, in production of transparency sheets for use in overhead projectors (OHPs). They are also unsuitable for use with currently available glossy media.

US Re 34933 concerns receiver sheets for use in offset lithography and similar printing techniques using solvent-based inks containing oil. The receiver sheets may comprise a transparent substrate, eg of transparent polyester such as polyethylene terephthalate, carrying a transparent ink-receptive polymeric layer comprising one or more polymers or copolymers, eg a copolymer of n-butyl methacrylate and isobutyl methacrylate. Such receiver sheets may be used to produce transparent printed images, eg by offset lithography. The receiver sheets are not, however, suited to use in ink jet printing using oil-based printing inks. For use with mechanical printing techniques, such as offset lithography, a receiver medium requires properties of mechanical stability and abrasion resistance that are not necessary when printing using ink jet techniques. Further, the solvent-based inks used for this purpose are rather different from oil-based ink jet printer inks, typically being high viscosity compositions with high solids content, and having a much smaller content of oil as compared with oil-based ink jet printer inks. These prior art receiver sheets are not capable of absorbing the high oil content of oil-based ink jet printer inks, nor of adequately coping with the low viscosity properties of such inks.

The present invention thus aims to provide a novel receiver medium suitable for use with ink jet printers using oil-based printing ink.

## Summary of the Invention

According to one aspect of the invention there is provided a receiver medium for use with oil-based ink jet printing ink, comprising a substrate having an ink-receiving surface bearing a coating of crosslinked polymer comprising polyalkene, the alkene having at least 4 carbon atoms.

Suitable polyalkenes are soft polymers, having low glass transition temperatures (Tgs), typically below –30°C, with the chains of the polymers being in a very mobile state. Polyalkenes having a low degree of crystallinity are preferred. The polymer chains are nonpolar and so have high compatibility with the oil of the ink. The polymers are thus able to absorb large quantities of oil (due to compatibility) rapidly (due to the mobile state of the

polymer chains). However, such polymers tend to be rubbery at best and possibly soft and sticky, which are undesirable characteristics. Further, absorption of oil from the ink, in use, has a plasticising effect on the polymer and reduces Tg, making the material softer and/or stickier. Crosslinking acts to stabilise the polymer, by forming a three-dimensional network and making the polymer harder, less sticky and more robust. However, crosslinking reduces the rate of oil uptake, which can be disadvantageous. Crosslinking also reduces the capacity for oil, although this is generally not of practical significance except at very high degrees of crosslinking as capacity is generally more than adequate. The degree of crosslinking of the polyalkene should thus be adjusted to give an appropriate balance of coating characteristics, with preferred coatings being able rapidly to absorb large quantities of oil on application of oil-based ink, having good pigment adhesion with the dispersed pigment being permanently fixed on the surface, and being reasonably robust and resistant to damage.

Because the coating is capable of absorbing oil, there is no need for the substrate itself to be able to absorb oil. By applying such a coating to non-absorbent substrates it is thus possible for oil-based inks to be printed successfully onto non-absorbent substrates such as glossy white film materials in a way that has not hitherto been possible. In preferred embodiments, the coatings are optically transparent and so can be used on transparent substrates eg for the production of transparency sheets for use in OHPs. The substrate may alternatively be of other materials including metal, plastics, wood etc, and materials having metallised or other non-absorbent finishes. There is, however, no need for the substrate to be non-absorbent, and the coating can be equally well applied to an absorbent substrate, including absorbent paper, card etc. In this event the substrate itself may also act to absorb some of the oil from ink applied in use, in which case the coating may be made thinner than would be required on a non-absorbent substrate.

It will thus be apparent that the substrate can be selected from a very wide range of materials.

The substrate is typically in the form of a film or sheet, but the physical form is not important as the coating can be applied to substrates of a wide variety of physical forms.

Typical substrate materials include polymeric materials having suitable properties including dimensional stability, optical transparency, translucency or opacity, tensile strength, adhesion characteristics, thermal stability, hardness etc for the intended purpose. Transparent polymeric substrate materials suitable for use in the production of transparencies include sheets or films of polyester eg poly(ethyleneterephthalate) (PET) such as Melinex (Melinex is a Trade Mark) or poly(ethylenenaphthalate) (PEN). Polycarbonate sheets may also be used for this purpose. Such transparent sheets typically have a thickness of about 50 to about 150μm. Other possible polymeric materials include polysulphones, polyvinyl chloride, polystyrene, polyimides, polyolefins, polymethyl methacrylate, cellulose esters such as cellulose acetate etc. A wide range of paper and card materials may also be used as the substrate.

The substrate may be pre-treated, eg in known manner, prior to application of the coating. For example, the substrate may be pre-treated with an adhesion-promoting priming layer, eg of parachlorometacresol (PCMC).

The alkene of the coating may be branched or straight chain.

The alkene is preferably substantially non-crystalline.

The alkene is preferably a diene, more preferably a 1,3 diene with buta-1,3-diene and isoprene being the currently preferred alkenes.

The polyalkene must be suitably functionalised to enable crosslinking, eg by inclusion of hydroxy groups, amino groups etc in known manner, for crosslinking in known manner. For example, hydroxy groups can be crosslinked using formaldehyde resin chemistry, eg using melamine-formaldehyde resin, or by use of polyfunctional isocyanates etc. The degree of crosslinking should be adjusted to give a coating with desired properties, as discussed above.

The chain length between crosslinks is suitable in the range 10 to 500 monomer units, preferably 20 to 200, and especially 30 to 100 units.

Good results have been obtained using Liquiflex H from Krahn Chemie (Liquiflex H is a Trade Mark) which is a hydroxy-ended polybutadiene of molecular weight about 2700 with one hydroxy group at each end of the molecule, ie having two hydroxy groups per molecule. Liquiflex H is a viscous liquid at room temperature. Liquiflex H can be readily crosslinked using melamine-formaldehyde resin, eg in the form of Cymel 303 from Dyno Cyanamid (Cymel 303 is a Trade Mark). Melamine-formaldehyde resin has 3 reactive functional groups and 3 less reactive functional groups, and is capable of providing appropriate crosslinking with the bifunctional hydroxy groups of Liquiflex H. Crosslinking can be readily performed in known manner, eg by mixing the materials with a suitable catalyst such as p-toluenesulphonic acid (PTSA) solution and curing the mixture for a suitable time at a suitable temperature to achieve a desired degree of crosslinking to produce a product having desired properties.

Using mixtures of Liquiflex H and Cymel 303 it was found appropriate to use Cymel 303 in an amount in the range 1 to30%, preferably 3 to15%, typically about 10%, based on the weight of Liquiflex H.

Good results have also been obtained using the polymer LIR-410 from Kuraray (LIR-410 is a Trade Mark) which comprises an isoprene backbone graft copolymerised with maleic monomethyl ester to give a material with a molecular weight of about 25,000. Functionality is provided by the residual acid groups on the maleic residues; there are 10 reactive groups per molecule. This material can similarly be readily crosslinked using melamine-formaldehyde resin, eg Cymel 303 as described above.

A mixture of alkenes may be used in production of the polyalkene. Additionally or alternatively, a mixture of polyalkenes may be used: in this case all the polyalkenes desirably have the same functional groups, eg hydroxy groups, for crosslinking purposes. For example, mixtures of two or more of hydroxy functionalised polybutadiene, styrene allyl alcohol copolymer (eg Scripset RJ101 from Monsanto (Scripset RJ101 is a Trade Mark)), styrene maleic anhydride copolymer (eg Scripset 550 from Monsanto (Scripset 550 is a Trade Mark)) and poly parahydroxystyrene (eg Lincur M from Maruzen Petrochemical Co (Lincur M is a Trade Mark) may be used and have been found to enhance pigment adhesion.

Suitable curing conditions (time and temperature) can be readily determined by experiment for any combination of chemicals and coating thickness. A curing temperature in the range 110 to 140°C, preferably in the range 120 to 130°C, is generally suitable, with curing times at up to 180 seconds generally being appropriate.

The coating materials may be applied by any suitable coating technique, including those known in the field, eg by use of a Meier bar, by roller coating, rod coating, slide coating, curtain coating, doctor coating etc.

The coating may be applied to the entire surface of the substrate or to only selected areas of the substrate surface. In the case of a sheet or film of substrate, the coating will typically be applied to at least one surface and possibly both surfaces (to enable double-sided printing).

The coating thickness will typically be 30 to 100μm for non-absorbent substrates, eg about 80μm, with thinner coatings, eg about 5μm, being suitable for absorbent coatings, with coating thickness being selected depending on substrate properties and desired characteristics of the receiver medium.

The coating desirably includes particulate filler material, to modify mechanical properties of the coating and in particular to enhance stiffness and rigidity, making the coating less soft. Suitable materials for this purpose include inorganic, organic or polymeric particulates such as silica including amorphous silica, crystalline silica, fumed silica, aluminium trihydrate, calcium carbonate, glass, clays, aluminium silicates, polyolefin particulates, organic pigments and mixtures thereof. It is preferred to use porous inorganic particulate material for this purpose, eg silica: in this event the porous filler material may also functional to absorb some of the oil from ink applied to the receiver medium. Particulate filler material has a tendency to increase light scattering, reducing coating transparency, so this factor must be taken into consideration in relation to transparent substrates and coatings, while being of no relevance to opaque receiver media. The particulate filler material may additionally act to increase surface roughness of the coating, thus reducing the tendency of the coating to block ie stick by wetting action to adjacent surfaces: this tendency arises from the low Tg of

the coating. Filler material particles suitably have a primary size in the range 5nm to 50µm. Fillers with a dimension much smaller than the wavelength of light can be used at higher loadings than larger fillers (because of their lower scattering) and therefore make a greater contribution to the mechanical properties of the coating, but are less efficient at creating surface roughness than are fillers with a major dimension of comparable size to the coating thickness. It is often desirable to incorporate fillers of two different sizes in order to optimise the overall properties of the coating.

The receiver medium may include an optional top coat (or supercoat) over the crosslinked polyalkene coating. A top coat desirably has the following characteristics:

1) The top coat should be capable of absorbing oil from applied oil-based ink reasonably rapidly.

2) The top coat should be of higher Tg than the coating so as to reduce the tendency of the receiver medium to block.

3) The top coat should exhibit good adhesion to pigment of applied ink.

The top coat conveniently comprises one or more polymers, and one example of a top coat formulation is a mixture of polybutadiene, styrene butadiene rubber and polystyrene.

The top coat is typically much thinner than the crosslinked polyalkene coating, eg having a thickness in the range 0.2 to 5µm.

The top coat desirably includes particulate filler material, eg as discussed above, to improve anti-blocking properties and possibly also to absorb oil and to improve pigment adhesion and other receiver medium properties. Where the receiver medium includes a top coat, possibly comprising particulate filler material, it may nevertheless be desirable to include particulate filler material in the crosslinked polyalkene coating to perform a stiffening function. Again the light-scattering effect of particulate filler materials must be born in mind when dealing with transparent receiver media. By use of a relatively thin top coat containing filler, the

anti-blocking effect can be maximised without introducing too much light scattering, as smaller particles (typically up to 10μm) can be used than would be required in the thicker crosslinked polyalkene coating, and the particles are concentrated near the surface of the assembly.

A top coat may be applied by any suitable coating technique, for example those discussed above in connection with the crosslinked polyalkene coating.

Other additives may optionally be included in the coating to improve properties of the coating. For example, lubricants and release agents, such as waxes and silicones, may be included to reduce friction and/or adhesion at the coating surface.

In a further aspect, the invention provides a method of making a receiver medium for use with oil-based ink jet printing ink, comprising applying to an ink-receiving surface of a substrate a coating of crosslinked polymer comprising polyalkene, the alkene having at least 4 carbon atoms.

The receiver medium is used by oil-based ink jet printing ink being applied thereto by an inkjet printing technique, eg in known manner, using known ink-jet printing apparatus. The ink may be, eg, generally as described in WO 96/24642 discussed above. On impingement on the receiver medium, the oil of the ink is rapidly absorbed by the ink-receiving surface (ie the coating of crosslinked polyalkene and possibly also by the top coat if present) and may also in part be absorbed by the substrate if absorbent, as discussed above.

In another aspect, the invention thus provides a method of printing, comprising applying oil-based ink to the ink-receiving surface of receiver medium in accordance with the invention by an ink jet printing technique.

The coatings described in the present application may optionally be used in conjunction with coatings described in the specifications of our co-pending UK application Nos. 9900489.7, 9900490.5 and 9900491.3. For example a polyisoprene emulsion coating as described in the

specification of application No. 9900490.5 may be applied over a crosslinked polyalkene coating as described in the present specification.

The invention will be further described, by way of illustration, in the following examples.

Examples

Samples of experimental receiver media were made and tested for their ability to absorb oil-based ink (comprising organic pigments dispersed in aliphatic hydrocarbon oil with oleyl alcohol, generally as described in WO 96/24642 by placing a few drops of ink on the edge of the coating, and drawing a Meier bar (24 μm unless otherwise stated) over the surface. The ink was then viewed obliquely in order to determine the drying time. The ability of the prints to withstand abrasion was also determined by drawing a rubber-gloved finger lightly over the printed area. Transparency was normally judged simply by looking at the samples, and this was confirmed from time to time by placing representative samples on an OHP.

Experiments were performed using Liquiflex H (a hydroxy-ended polybutadiene of molecular weight about 2700, with two hydroxyl groups per molecule) crosslinked using Cymel 303 melamine-formaldehyde resin, on transparent PET film.

Initial experiments showed that around 1 to 30% by weight of Cymel 303 resin based on the weight of Liquiflex was required in order to obtain a rubbery rather than a sticky film from Liquiflex coatings in a reasonable cure time. They also showed that rapid drying times could be achieved, but that the pigment layer was very easily wiped from the surface, even some days after printing. The lower Cymel contents gave lightly crosslinked coatings, which were extremely soft and easily damaged, and blocked readily against any smooth surface. High Cymel contents increased the crosslinking and toughened the materials, but reduced the rate of ink uptake, without increasing the abrasion resistance of the ink after drying. The preferred range of Cymel content is 3 to 15%. Adding some silica to the formulation hardened the coating without a great reduction in the rate of absorption.

Example 1 – Crosslinked polybutadiene applied from solution.

Liquiflex stock solution A:

| | | | |
|---|---|---|---|
| Liquiflex H | 33 g | hydroxylated polybutadiene | Krahn Chemie |
| Cymel 303 | 3.3 g | melamine formaldehyde | Dyno Cyanamid |
| Aerosil 380 | 0.5 g | Fumed silica | Degussa |
| Toluene | 30 g | | |

PTSA solution:

| | |
|---|---|
| p-toluenesulphonic acid | 1 g |
| Toluene | 5 g |
| Butan-2-one | 5 g |

A mixture of Liquiflex stock solution A (5 g) and PTSA crosslinking catalyst solution (0.2 g) was coated onto Melinex O transparent PET film using a 150 μm Meier bar and cured in an oven at 130 °C for 60 seconds. This produced a coating about 80μm thick, after solvent evaporation. The resultant receiver medium was tested with magenta ink, by the technique described above. A 12 μm layer dried in 30 to 35 seconds; a 24 μm layer dried in 70 to 100 seconds.

When the cure temperature was reduced to 120 °C with a cure time of 120 seconds, the drying time of a 24 μm layer of magenta ink was 30 to 35 seconds, and the film showed good absorption and control of ink when tested on a laboratory ink jet printer.

Example 2

A mixture of Liquiflex stock solution A (5 g) and PTSA solution (0.2 g) was coated onto Melinex O PET film using a 150 μm Meier bar and cured in an oven at 120 °C with a cure time of 120 seconds. The drying time of a 24 μm layer of magenta ink was 70 to 90 seconds.

All the above coatings had a soft rubbery feel, the coatings with the best absorption being the softest. All of the prints were susceptible to abrasion damage.

Example 3

A solution as follows:

| | |
|---|---|
| Liquiflex H | 13 g |
| Scripset RJ101 | 1.3 g (Styrene Allyl Alcohol copolymer, Monsanto) |
| Cymel 303 | 0.5 g |
| PK3 | 1.0g (Di n Butylamine salt of pTSA, 28% w/w in Methanol from ICI Imagedata) |

dissolved in 13 g of butan-2-one/Toluene, 1:1 was coated with a 100 μm Meier bar and cured for 1800 seconds at 130 °C. The resultant coating was of low tack and slightly hazy. Ink drying time was about 2 minutes but with much better pigment adhesion compared with the previous examples. Experiments using Scripset 550 and Lincur M in place of Scripset RJ101 produced similar results. Scripset 550 is a styrene maleic anhydride copolymer from Monsanto. Lincur M is poly parahydroxystyrene from Maruzen Petrochemical Co. Scripset 550 and Lincur M are Trade Marks.

Example 4 - Supercoated formulations

A solution of polybutadiene (BR55 from Krahn Chemie)/ styrene butadiene rubber (Cariflex TR1101 from Shell Chemical Company) (Cariflex TR1101 is a Trade Mark)/ polystyrene (molecular weight about 6000) in proportions of 40/40/20, at 4% solids in 1:1 butan-2-one/ toluene was coated with a 36 μm (K4) Meier bar as a supercoat on top of a coating as described in Example 2. This gave a coating that still showed signs of wetting and intimate contact to a piece of uncoated Melinex O but released more easily and without marking than the unmodified Liquiflex. Pigment adhesion was not significantly affected.

This system was then further modified by the inclusion of various different additives. Additive was added in an amount of 5% w/w of the weight of the supercoat. The supercoat formulations containing additive were again coated onto a coating as described in Example 2 using a K4 Meier bar and cured for 30 seconds at 110°C. The additives used were soluble

lubricants/release agents, the function of which is to reduce friction and reduce adhesion of the coating surface while not modifying the surface roughness of the coating. Results of these were as follows:

Paraffin wax, melting point. 50°C - No effect

Crodamide ER (erucaminde wax, from Croda (Crodamide ER is a Trade Mark)) -Improved pigment adhesion

Tegomer 6440 (copoly dimethylsiloxane caprolactone from Tego Chemie (Tegomer 6440 is a Trade Mark)) - Improved pigment adhesion and lowered friction and easier release.

A further enhancement of the surface handleability was made by the addition of 2.5% w/w Fluo HT (micronised polytetrafluoroethylene, mean diameter 2μm, from Micropowders Inc. (Fluo HT is a Trade Mark)) on solids of the supercoat.

Example 5

Samples were then made up by using a 100 μm layer of a base coat formulation (made by mixing together the ingredients as specified in the table below) onto clear unprimed Melinex O and curing for 180 seconds at 130 °C.

A supercoat formulation (made by mixing together the ingredients as specified in the table below) was coated with a 36 μm Meier bar onto the base coat, followed by drying for 30 seconds at 130 °C.

Base Coat Formulation

| Component | Weight | Description | Manufacturer |
|---|---|---|---|
| Liquiflex H | 13g | | |
| Cymel 303 | 0.5g | | |
| pTSA | 0.3g | | |
| Microperl 050 20 | 0.26g | solid glass spheres, mean 20 μm | Sovitec S.A. Belgium |
| Butan-2-one | 6.5g | | |
| Toluene | 6.5g | | |

Supercoat formulation

| Component | Weight | Description | Manufacturer |
|---|---|---|---|
| BR55 | 1.6g | Polybutadiene | Krahn |
| Cariflex TR1101 | 1.6g | Styrene butadiene co-polymer | Shell Chem. Co. |
| Polystyrene | 1.0g | M Wt. 6000 | Polysciences |
| Tegomer 6440 | 0.2g | Copoly dimethyl siloxane caprolactone | Tego Chemie |
| Fluo HT | 0.1g | Micronised PTFE, mean 2µm | Micropowders Inc. |
| Butan-2-one | 50g | | |
| Toluene | 50g | | |

The supercoat did not affect drying time, but reduced the tack.

Example 6

Further experiments were carried out using the polymer LIR-410 (from Kuraray) in place of Liquiflex H. LIR-410 comprises an isoprene backbone (in place of the butadiene backbone of Liquiflex H) and is graft copolymerised with maleic monomethyl ester to give a material with a molecular weight of about 25,000. Functionality is provided by residual carboxylic acid groups on the maleic residues; there are 10 reactive groups per molecule.

A solution was made up as follows:

| | |
|---|---|
| LIR-410 | 5.5g |
| Toluene | 4.5g |
| Cymel 303 | 0.7g |
| PTSA | 0.25g |

This was coated onto Melinex O transparent PET film using a 50µm wet weighter Meier bar, and cured in an oven at 130°C for 180 seconds.

The resulting coating was slightly hazy, but projected well. The coating was not as soft as the Liquiflex-based coatings, and did not block against Melinex even in the absence of silica. A 24 μm application of magenta ink dried in 50 seconds.

Claims

1. A receiver medium for use with oil-based ink jet printing ink, comprising a substrate having an ink-receiving surface bearing a coating of crosslinked polymer comprising polyalkene, the alkene having at least 4 carbon atoms.

2. A receiver medium according to claim 1, wherein the substrate comprises a film or sheet of transparent material.

3. A receiver medium according to claim 2, wherein the substrate comprises polyethylene terephthalate.

4. A receiver medium according to claim 1, wherein the substrate is capable of absorbing oil.

5. A receiver medium according to any one of the preceding claims, wherein the polyalkene has a glass transition temperature of less than –30°C.

6. A receiver medium according to any one of the preceding claims, wherein the alkene is substantially non-crystalline.

7. A receiver medium according to any one of the preceding claims, wherein the alkene is a diene.

8. A receiver medium according to claim 7, wherein the diene is a 1,3-diene.

9. A receiver medium according to claim 8, wherein the diene is buta-1,3-diene or isoprene.

10. A receiver medium according to any one of the preceding claims, wherein the polyalkene includes one or more of hydroxy groups and amino groups.

11. A receiver medium according to any one of the preceding claims, wherein the polyalkene is crosslinked using melamine-formaldehyde resin.

12. A receiver medium according to any one of the preceding claims, comprising hydroxy-ended polybutadiene crosslinked using melamine-formaldehyde resin.

13. A receiver medium according to claim 12, wherein the melamine-formaldehyde resin is used in an amount in the range 1 to 30%, preferably 3 to 15%, based on the weight of polybutadiene.

14. A receiver medium according to any one of the preceding claims, wherein the coating includes particulate filler material.

15. A receiver medium according to any one of the preceding claims, further comprising a top coat over the crosslinked polyalkene coating.

16. A receiver medium according to claim 15, wherein the top coat includes particulate filler material.

17 A method of making a receiver medium for use with oil-based ink jet printing ink, comprising applying to an ink-receiving surface of a substrate a coating of crosslinked polymer comprising polyalkene, the alkene having at least 4 carbon atoms.

18. A method of printing, comprising applying oil-based ink to the ink-receiving surface of a receiver medium in accordance with any one of claims 1 to 16 by an ink jet printing technique.

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/04347

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 4 559 256 A (MATSUMOTO FUMIO) 17 December 1985 (1985-12-17) claim 1; examples 3,4 | 1-3,7-9 |
| X | PATENT ABSTRACTS OF JAPAN vol. 014, no. 266 (M-0982), 8 June 1990 (1990-06-08) & JP 02 076775 A (MATSUSHITA ELECTRIC IND CO LTD), 16 March 1990 (1990-03-16) abstract | 1,7-9, 14,17,18 |
| X | EP 0 698 638 A (SHELL INT RESEARCH) 28 February 1996 (1996-02-28) claims; examples | 1 |
| X | US 5 688 598 A (ALLMAN JACK C ET AL) 18 November 1997 (1997-11-18) claim 1 | 1 |

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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| European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016 | Heywood, C |

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International Application No
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